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DISPERSIONS CONTAINING LIVING RADICALS

10 **CROSS REFERENCE TO RELATED APPLICATIONS**

This application claims the benefit of United States Provisional Application No. 60/404,557, filed 19 August 2002.

FIELD OF THE INVENTION

15   The invention relates to a dispersion of polymer particle, where the polymer particles contain, on average, more than one living radical per particle, where the living radicals are not chemically protected. The living radicals can then be used to form polymers with a controlled architecture.

20 **BACKGROUND OF THE INVENTION**

Free radical polymerization is a preferred technique in the synthesis of many polymers. One drawback of free radical polymerization is the lack of control over the polymer architecture produced. The type and amount of initiator, temperature, and delayed monomer feeds have all been used to control the final structure and size of the polymer particles.

25   Living polymers offer some control of the polymer structure. Living polymers are polymers having an active/ growing end on a polymer chain (non-terminated polymer chain). Most commonly, living ends are formed by anionic polymerization in non-polar solvent, or involve a capping-mechanism to stop a growing free radical, then restarting the polymer growth by reversible removal of the cap.

Chemical trapping agents are known in the art as a means of capping a living polymer radical by a reversible means, then uncapping the living radical for latter continued polymerization. Unfortunately such a method requires additional purification costs to remove the trapping agent from the product. The trapping agents also add kinetic limitations, dependent on the specific trapping agent used.

U.S. Patent 5,173,551 and "Studies of the Polymerization of Methacrylic Acid via Free-Radical Retrograde Precipitation Polymerization Process", J. Applied Polymer Science, Vol. 62, 2039-2051 (1996) describe the use of a free-radical retrograde polymerization process as a means of controlling the polymer molecular weight distribution. In this process a monomer mixture in a solvent is initiated by a solvent-soluble free radical initiator to produce polymer radicals that precipitate into polymer-rich phases in a solvent. The above patent also addresses the capability of FRRPP to control the activity of polymer radicals and use them to produce copolymers. Additionally it provides a detailed description of the original process, a possible apparatus for running it, and ways of regulating the rate of reaction through changing temperature and adding or removing monomers or inert diluents.

U.S. Patent Applications 10/045881 and 10/045725 describe free radical dispersions and copolymers that can be made by free radical retrograde precipitation.
One drawback of FRRPP is that it requires poor solvents that precipitate a polymer above the lower critical solution temperature.

There is a need for a method to control polymer architecture, without the drawbacks found in the current art.

Surprisingly it has been found that a stable dispersion of particles containing particles having an average of more than one living radical per particle can be produced without chemical capping agents or mediation, and without the need to produce said radicals through a free radical retrograde precipitation polymerization process.

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SUMMARY OF THE INVENTION

The present invention is directed to a dispersion of polymer particles, the particle containing, on average, more than 1 living radicals each, the radicals not being chemically protected. The invention is also directed to a free radical polymerization process resulting in a

10   dispersion containing polymer particles having on average one or more living radicals. The process involves carefully regulating the polymerization conditions to under monomer-starved conditions, to produce small size particles containing, on average, more than one living radical. These living polymer radicals can be further reacted with additional monomer(s), either the same monomer to increase the polymer molecular weight, or another monomer or monomers to form

15   block copolymers, tapered block polymers, or controlled architecture compositions. The additional polymerization(s) occur without the need for additional initiator.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a chart of particle size evolution.

20   Figure 2 is a GPC curve representing six different samples

Figure 3 is a GPC curve representing six different samples

Figure 4 is a GPC curve representing four different samples.

Figure 5 is GPC curve representing four different samples.

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DETAILED DESCRIPTION OF THE INVENTION

5   As used herein, the term "dispersion" is used to mean a continuous phase having within it a

dispersed phase. The dispersed phase exists as discreet domains or particles and may be

stabilized, if necessary, by a surfactant or stabilizer. The is used to apply to many possible

material compositions, including, but not limited to, emulsions, mini-emulsions, micro-

emulsions, precipitation, colloidal dispersions, and colloidal suspensions.

10   The term "stabilizer" as used herein, means surfactants, stabilizers, and other dispersion

aids.

         While not being bound by any particular theory, it is believed that the small particle size,

plus careful control of initiator and monomer additions produces stable particles with radicals

trapped inside. Due to the small particle size, the radicals are sterically hindered, resulting in

15   very reduced rates of termination.

         The process for producing the polymer dispersion of the present invention involves

carefully regulating polymerization conditions to create and maintain small particles containing

trapped radicals. This is accomplished by carefully regulating the initiator, monomer, and

stabilizer concentrations. This allows for a maximization of particle nucleation and a

20   minimization of particle size. The polymer dispersions of the present invention generally have

water as the continuous phase. A continuous phase of a mixed aqueous solvent, such as

water/miscible alcohol could also be used. Additionally, an inverse emulsion process could also

be employed. The general description and examples which follow describe primarily a water-

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continuous phase. Those of skill in the art can apply the same concepts and techniques to other polymerization systems.

In the first stage of the polymerization, water, stabilizer, and free radical initiator are added to the reactor, and conditions are adjusted for the production of free-radicals. The radicals may be generated by thermal, redox, U.V., gamma radiation, or other method, depending on the initiator system chosen. Following formation of free radicals, the monomer feed is added, maintaining a monomer-starved condition. The reaction will become initiator starved toward the latter of the initial reaction stage.

The first phase of the polymerization results in a dispersion of polymer particles in the dispersing medium, preferably water. Each polymer particle contains on average one or more living polymer radicals. Preferably the particles contain on average at least 2 living polymer radicals, more preferably at least 5 living polymer radicals, even more preferably at least 10 living polymer radicals, and most preferably at least 20 living polymer radicals. Particles having over 100, 1000, or even 10,000 and more living polymer radicals per polymer particle have been produced. The living polymer particles of the present invention exist without chemical capping agents which are known in the art and which are added to temporarily protect the living radical. The temporary chemical capping agents are then reversible to expose the living radical.

The living radicals trapped in the particles of the dispersion under thermal initiation conditions remain for a period of longer than seven initiator half-lives, and preferably for at least 15 hours, and most preferably for more than a few days. Trapped living radicals in redox and other initiator systems are also long lived – remaining for at least 10 minutes

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Once the dispersed monomer has reacted to near 100 percent, generally up to 5 to 10 initiator half lives, additional monomer can then be added to the polymer particles containing multiple living radicals. In the case of addition of the same monomer, polymer of a higher molecular weight will be formed. Since termination of the particles is controlled, the polymer molecular weight can be controlled to produce any desired molecular weight, with molecular weights of greater than 3,000,000 possible. The additional monomer can also be one or more different monomers, leading to the formation of a block copolymer. The process of the invention can produce a pure block copolymer, since virtually all of the first stage monomer should be consumed prior to introduction of the second monomer. The second stage monomer can advantageously be quite different than the first stage monomer, as in the case where one monomer is hydrophilic and the other hydrophobic. Amphiphilc block copolymers and novel block copolymer combinations are possible using the process of the present invention. The process is not limited by reactivity ratios, but is rather limited only by diffusion. Tapered polymer compositions can also be produced by the control over the reaction offered by the process of the invention.

The process of adding additional monomer may be continued for any number of stages, without the need for additional initiator.

Monomers useful in the present invention include any monomer that can undergo free radical chain polymerization. Especially useful monomers are ethylenically unsaturated monomers. Examples include (meth)acrylates; maleates; vinyl esters; itaconates; vinyl ethers; styrenics; unsaturated hydrocarbons; nitrogen functional monomers such as acrylonitrile, alkyl acrylamides n-vinyl formamide, vinyl pyrrolidone, zwitterionic or ampholytic monomers; hydroxyl-functional monomers;macromers; (meth)acrylic acid, and N-caprolactam. The term

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(meth) acrylates, as used herein, refers to both acrylate as well as methacrylate monomers and their derivatives. Similarly, the term (meth)acrylic acids refers to acrylic acid, methacrylic acid and their derivatives. Low levels of crosslinking monomers may also be used as known in the art to improve certain properties of the polymers.

5   The initial charge may optionally contain a polymer latex seed. It is believed that the use of a polymer latex seed can be advantageous for trapping initiated polymer radicals. The seed may be formed in situ by introducing a small amount of monomer into the initial charge, and polymerizing said monomer prior to the commencement of the delayed monomer feed.

          The dispersion may be stabilized by means of a surfactant, stabilizer, other dispersion

10   aids and dispersants, or a mixture thereof. Surfactants useful in the present invention include anionic, non-ionic, cationic and amphoteric surfactants. Preferred surfactants are non-ionic, such as alkyl phenol ethoxylates, alkyl ethoxylates, or other ethoxylates. Other surfactants include, but are not limited to alkyl phenol, alkyl sulfate, ether sulfate, phosphate ester, and similar anionic surfactants. Stabilizers can be either polymeric or non-polymeric and include, but are

15   not limited to polyvinyl alcohols, and amphiphilic block copolymer stabilizers. Polymeric dispersants include but are not limited to, poly(maleic acid) and copolymers of maleic acid with compatible ethylenically unsaturated monomers such as mono- and diesters of maleic acid, (meth)acrylic acid, alkyl esters of (meth)acrylic acid, hydroxyalkyl esters of (meth)acrylic acid, alpha-methyl styrene, styrene, and derivatives thereof, vinyl acetate, crotonic acid, esters of

20   crotonic acid, and acrylamide, and derivatives thereof. Other suitable linear polymeric dispersants include, but are not limited to, polystyrene sulfonates, which are typically obtained by sulfonating poly(styrene) or copolymers of styrene with compatible ethylenically unsaturated monomers including, but not limited to, (meth)acrylic acid, esters of (meth)acrylic acid, maleic

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acid, and mono- and diesters of maleic acid; condensates including but not limited to naphthalenesulfonic acid-formaldehyde condensate and melamine-formaldehyde condensate. Certain natural or naturally derived polymers useful in the present invention include but are not limited to tannins, lignins, lignosulfates, alginates, dispersed or soluble starches and modified

5   starches, and cellulosic polymers. Other stabilizing and dispersing aids may include copolymerizable compounds, such as sodium vinyl sulfonate, that may help in the stabilization. A mixture of one or more surfactants, stabilizers, dispersants, or a combination of surfactants and stabilizers is also useful in the invention.

The polymerization occurs due to free radical initiation. The free-radical generating

10   agent is capable of generating free radicals to initiate polymerization by the use of one or more mechanisms such as photochemical initiation, thermal initiation, redox initiation, degradative initiation, ultrasonic initiation, U.V. initiation, gamma ray initiation, or the like. Preferably the initiators are selected from azo-type initiators, peroxide type initiators, or mixtures thereof. Examples of suitable peroxide initiators include, but are not limited to, diacyl peroxides, peroxy

15   esters, peroxy ketals, dialkyl peroxides, and hydroperoxides, specifically benzoyl peroxide, deconoyl peroxide, lauroyl peroxide, succinic acid peroxide, cumene hydroperoxide, t-butyl peroxy acetate, 2,2-di (t-butyl peroxy) butane diallyl peroxide), cumyl peroxide, or mixtures thereof. Examples of suitable azo-type initiators include, but are not limited to azobisisobutyronitrile (AIBN), 1,1'-azobis (1-cyclohexane carbonitrile), acid-functional azo-type

20   initiators such as 4,4'-azobis (4-cyanopentanoic acid. Preferably the dispersing agent is water, and the free-radical generating agent is a water-soluble initiator, such as 2,2'-Azobis (N,N'-amidinopropane) dihydrochloride or 2,2'-Azobis (N,N'-dimethyleneisobutyramidine)

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dihydrochloride. The free radicals react with monomer present in equilibrium amounts in the aqueous phase to form polymer chains.

The reaction of the present invention is not limited by reactor geometry. The reaction may be a batch polymerization, semi-batch polymerization, or a continuous polymerization such as in a tubular reactor. The polymerization may occur at atmospheric pressure, or at elevated pressure.

The control mechanism of the polymerization is not critically effected by the glass transition temperature of the polymer product.

Particle size can be controlled by the type and amount of surfactant or stabilizer used as well as during the making and processing of the dispersion. The particle size is kept very small. While not being bound to any particular theory, it is believed that the radicals remain living in part due to being sterically hindered within a small particle. The average particle size in the first stage is preferably from 1 to 200 nanometers, more preferably from 10 to 150 nanometers. The particle size distribution can be adjusted from a relatively broad and multi-modal distribution, to a nearly unimodal distribution. The particle size in the second stage is generally greater than 100 nanometers, and may be up to several microns.

The solids levels of the copolymer dispersions can be in the range of from 5 to 50 percent by weight, and preferably from 10 to 30 percent by weight.

Termination of the polymer radicals can be accomplished by one or more steps such as reducing the temperature of the reaction chamber, increasing the pressure within the reaction chamber; adding a suitable solvent for the resulting polymer; adding a suitable chain transfer agent (e.g., a mercaptan type agent) to the system; or by introducing a suitable radical scavenger (e.g., oxygen).

The polymerization method may be used to produce high molecular weight homopolymers, and block copolymer architectures including di-blocks, tri-blocks, and tapered blocks. The composition of the blocks can be tailored by adjusting the compositions of the monomer feeds. Other polymer architectures which may be produced include, but are not

5   limited to, multiblocks, comb structures, blocky-grafts, difunctional initiation polymers, and radial polymers.

Polymer dispersions produced by the present invention may be used in adhesives, paints, industrial coatings, inks, film-formers, polymeric surfactants, stabilizers, tougheners, binders, non-woven materials, specialty additives, rheology modifiers, thermoplastic elastomers,

10   polymeric compatibilizers, bio-adhesives, encapsulants for controlled release, nanoparticles, nanogels, redispersible powders, membranes, organic-inorganic composites, porous membranes, structural polymers, engineered plastics, breathable membranes, medical implants, bio-compatable polymers, and a variety of other commercial applications.

The method of the invention allows for economical production of copolymers that are

15   difficult to obtain by other means, such as, but not limited to, polyvinyl acetate-bloc-polystyrene, polyvinyl ethers – block- polystyrene, polyvinyl esters-block-poly(meth)acrylates such as polyvinyl acetate – block – polymethylmethacrylate.

The following examples are presented to further illustrate and explain the present invention and should not be taken as limiting in any regard. The emulsion was stable at room

20   temperature with no creaming or settling obvious even after one year. The copolymers obtained were characterized using thermal analysis (differential scanning calorimetry) and fractionation/ solvent extraction to verify their blocky structure.

Example I

Stage I: Water (150 mL), surfactant (sodium dodecyl sulfate, Rhodia) (3 g.), and initiator (0.3 g.) (2,2"-Azobis (N,N'-amidinopropane) dihydrochloride or V-50, Wako chemicals) in a 4 necked round bottom flask were purged with nitrogen for 45 min. Uninhibited styrene monomer (33 mL) in a slow add funnel was purged with subsurface nitrogen for 30 min. Reaction mixture was heated to 80 °C while stirring over 20 min. At 50 °C (7 mL) of styrene monomer was slow added over 5 min and remaining monomer was slow added over 3 hours.

Stage II: Reaction mixture was cooled to 60 °C. A pre-emulsion was made by adding uninhibited butyl acrylate (78.3 mL) dropwise to a beaker containing water (25 mL), and surfactant (sodium dodecyl sulfate, Rhodia) (2.1 g.) while mixing very vigorously using a mixer. The pre-emulsion was purged with nitrogen for 30 min in a slow addition funnel and slow added over 1 hour at 60 °C. Reaction mixture was stirred for 3 hours at 60 °C and then was cooled to room temperature.

Example II

Stage I: Water (150 mL), surfactant (sodium dodecyl sulfate, Rhodia) (3 g.), and initiator (0.3 g.) (2,2"-Azobis (N,N'-amidinopropane) dihydrochloride or V-50, Wako chemicals) in a 4 necked round bottom flask were purged with nitrogen for 45 min. Uninhibited styrene monomer (33 mL) in a slow add funnel was purged with subsurface nitrogen for 30 min. Reaction mixture was heated to 80 °C while stirring over 20 min. At 50 °C (7 mL) of styrene monomer was slow added over 5 min and remaining monomer was slow added over 3 hours.

Stage II: Reaction mixture was cooled to 60 °C. A pre-emulsion was made by adding uninhibited styrene (77.0 mL) dropwise to a beaker containing water (25 mL), and surfactant

(sodium dodecyl sulfate, Rhodia) (2.1 g.) while mixing very vigorously using a mixer. The pre-emulsion was purged with nitrogen for 30 min in a slow addition funnel and slow added over 1 hour at 60 °C. Reaction mixture was stirred for 3 hours at 60 °C and then was cooled to room temperature.

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Example III

Stage I: Water (150 mL), surfactant (sodium dodecyl sulfate, Rhodia) (3 g.), and initiator (0.3 g.) (2,2"-Azobis (N,N'-amidinopropane) dihydrochloride or V-50, Wako chemicals) in a 4 necked round bottom flask were purged with nitrogen for 45 min. A mixture of uninhibited styrene and

10 methacrylic acid monomer (35 mL) in a slow add funnel was purged with subsurface nitrogen for 30 min. Reaction mixture was heated to 80 °C while stirring over 20 min. At 50 °C (7 mL) of monomer mix was slow added over 5 min and remaining monomer was slow added over 3 hours.

Stage II: Reaction mixture was cooled to 60 °C. A pre-emulsion was made by adding

15 uninhibited butyl acrylate (78.3 mL) dropwise to a beaker containing water (25 mL), and surfactant (sodium dodecyl sulfate, Rhodia) (2.1 g.) while mixing very vigorously using a mixer. The pre-emulsion was purged with nitrogen for 30 min in a slow addition funnel and slow added over 1 hour at 60 °C. Reaction mixture was stirred for 3 hours at 60 °C and then was cooled to room temperature.

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Example IV

Stage I: Water (150 mL), surfactant (sodium dodecyl sulfate, Rhodia) (3 g.), and initiator (0.3 g.)

(2,2'-azobis[2-(2-imidazolin-2-yl) propane] dihydrochloride or VA-044, Wako chemicals) in a 4

necked round bottom flask were purged with nitrogen for 45 min. Uninhibited styrene monomer

5   (35 mL) in a slow add funnel was purged with subsurface nitrogen for 30 min. Reaction mixture

was heated to 65 °C while stirring over 20 min. At 50 °C (7 mL) of styrene monomer was slow

added over 5 min and remaining monomer was slow added over 3 hours.

Stage II: Reaction mixture was cooled to 60 °C. A pre-emulsion was made by adding

uninhibited butyl acrylate (78.3 mL) dropwise to a beaker containing water (25 mL), and

10   surfactant (sodium dodecyl sulfate, Rhodia) (2.1 g.) while mixing very vigorously using a mixer.

The pre-emulsion was purged with nitrogen for 30 min in a slow addition funnel and slow added

over 1 hour at 60 °C. Reaction mixture was stirred for 3 hours at 60 °C and then was cooled to

room temperature.

15   **Example V**

Stage I: Water (203 mL), surfactant (Igepal CA-897 Octylphenol ethoxylate, Rhodia)

(2.9 g.), and initiator (0.2 g.) (2,2'-azobis[2-(2-imidazolin-2-yl) propane] dihydrochloride or VA-

044, Wako chemicals) in a 4 necked round bottom flask were purged with nitrogen for 45 min.

Uninhibited styrene (31 mL) in a slow addition funnel was purged with subsurface nitrogen for

20   30 min. At room temperature styrene monomer slow addition was started and 3 mL styrene was

slow added over 5 min. Reaction mixture was heated to 75 °C while stirring over 15 min.

Remaining monomer was slow added over 1.5 hours. At the end of styrene slow addition,

reaction mixture was stirred for 1.5 hours while cooling to 60 °C.

Stage II: Uninhibited styrene (30 mL) was purged with nitrogen for 30 min in a slow addition funnel and slow added over 2 hours at 60 °C. Reaction mixture was stirred for 1 hour at 60 °C and then was cooled to room temperature.

5   **Example VI**

Stage I: Water (200 mL), surfactant (Igepal CA-897 Octylphenol ethoxylate, Rhodia) (3.9g.), and initiator (0.1 g.) (2,2"-Azobis (N,N'-amidinopropane) dihydrochloride or V-50, Wako chemicals) in a 4 necked round bottom flask were purged with nitrogen for 45 min. Uninhibited styrene (21 mL) in a slow addition funnel was purged with subsurface nitrogen for 30 min. At

10   room temperature styrene monomer slow addition was started. Reaction mixture was heated to 80 °C while stirring over 10 min, 5 mL styrene was slow added over 10 min before reaction temperature reached 80 °C and remaining monomer was slow added over 1.5 hours. At the end of styrene slow addition, reaction mixture was stirred at 80 °C for 1.5 hours. Samples were taken at irregular intervals to determine conversion and molecular weight.

15   **Stage II:** Reaction mixture was cooled to 60 °C. Uninhibited styrene (36 mL) was purged with nitrogen for 30 min in a slow addition funnel and slow added over 2 hours at 60 °C. Reaction mixture was stirred for 2 hours at 60 °C and then was cooled to room temperature. Samples were taken periodically to determine conversion and molecular weight.

20   **Example VII (25D)**

Stage I: Water (175 mL), surfactant (sodium dodecyl sulfate, Rhodia) (2.5 g.), and initiator (0.5 g.) (2,2"-Azobis (N,N'-amidinopropane) dihydrochloride or V-50, Wako chemicals) in a 4 necked round bottom flask were purged with nitrogen for 45 min. Uninhibited styrene (55 mL)

in a slow addition funnel was purged with subsurface nitrogen for 30 min. Reaction mixture was heated to 80 °C while stirring over 20 min. At 50 °C (7 mL) of monomer mix was slow added over 5 min and remaining monomer was slow added over 3 hours.

Stage II: Reaction mixture was cooled to 60 °C. Uninhibited styrene (55 mL) was purged with

5   nitrogen for 30 min in a slow addition funnel and slow added over 1 hour at 60 °C. Reaction mixture was stirred for 3 hours at 60 °C and then was cooled to room temperature.

Example VIII (108)

Stage I: Water (200 mL), surfactant (Igepal CA-897 Octylphenol ethoxylate, Rhodia) (3.9g.),

10   and initiator (0.1 g.) (2,2"-Azobis (N,N'-amidinopropane) dihydrochloride or V-50, Wako chemicals) in a 4 necked round bottom flask were purged with nitrogen for 45 min. Uninhibited styrene (20.7 mL) in a slow addition funnel was purged with subsurface nitrogen for 30 min. At room temperature styrene monomer slow addition was started while heating to 80 °C and 5 mL styrene was slow added over 20 min before reaction temperature reached 80 °C and remaining

15   monomer was slow added over 1.5 hours. At the end of styrene slow addition, reaction mixture was stirred at 80 °C for 30 min.

Stage II: Reaction mixture was cooled to 60 °C. Uninhibited styrene (35 mL) was purged with nitrogen for 30 min in a slow addition funnel and slow added over 2 hours at 60 °C. Reaction mixture was stirred for 2 hours at 60 °C and then was cooled to room temperature.

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Example IX (137)

Stage I: Water (200 mL), surfactant (Igepal CA-897 Octylphenol ethoxylate, Rhodia) (3.9g.), and initiator (0.19 g.) (2,2"-Azobis (N,N'-amidinopropane) dihydrochloride or V-50, Wako

chemicals) in a 4 necked round bottom flask were purged with nitrogen for 45 min. Uninhibited vinyl acetate (21 mL) in a slow addition funnel was purged with subsurface nitrogen for 30 min. At room temperature vinyl acetate monomer slow addition was started while heating to 80 °C. Five mL vinyl acetate was slow added over 20 min before reaction temperature reached 80 °C and remaining monomer was slow added over 1.5 hours. At the end of monomer slow addition, reaction mixture was stirred at 80 °C for 30 min.

Stage II: Reaction mixture was cooled to 60 °C. Uninhibited styrene (41 mL) was purged with nitrogen for 30 min in a slow addition funnel and slow added over 2 hours at 60 °C. Reaction mixture was stirred for 2 hours at 60 °C and then was cooled to room temperature.

Example X

Stage I: Water (200 mL), surfactant (sodium dodecyl sulfate, Rhodia) (5.1g.), and initiator (0.3 g.) (2,2"-Azobis (N,N'-amidinopropane) dihydrochloride or V-50, Wako chemicals) in a 4 necked round bottom flask were purged with nitrogen for 45 min. Uninhibited methyl methacrylate (33 mL) in a slow addition funnel was purged with subsurface nitrogen for 30 min. At room temperature methyl methacrylate (MMA) monomer slow addition was started while heating to 80 °C. Three mL MMA was added to the flask in 5 min before the temperature reached 80 °C and the remaining monomer was slow added over 2.5 hours. At the end of monomer slow addition, reaction mixture was stirred at 80 °C for 30 min.

Stage II: Reaction mixture was cooled to 60 °C. Uninhibited n-butyl acrylate (78 mL) was purged with nitrogen for 30 min in a slow addition funnel and slow added over 1 hour at 60 °C. Reaction mixture was stirred for 2 hours at 60 °C and then was cooled to room temperature.

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Examples XI and XII show the impact of residual inhibitor from the monomer stock on second

stage monomer conversion. Example XI used monomer with a higher level of inhibitor than

example XII. It can be seen that second stage conversion was not observed in example XI (Table

5   I).

Example XI

Stage I: Water (200 mL), surfactant (Igepal CA-897 Octylphenol ethoxylate, Rhodia)

(4.2 g.), and initiator (0.1 g.) (2,2"-Azobis (N,N'-amidinopropane) dihydrochloride or V-50,

10   Wako chemicals) in a 4 necked round bottom flask were purged with nitrogen for 45 min.

Uninhibited styrene (21 mL) in a slow addition funnel was purged with subsurface nitrogen for

30 min. Reaction mixture was heated to 80 °C while stirring over 20 min. At room temperature

styrene monomer slow addition was started and 5 mL styrene was slow added over 10 min

before reaction temperature reached 80 °C and remaining monomer was slow added over 1.5

15   hours. At the end of styrene slow addition, reaction mixture was stirred at 80 °C for 30 min.

Stage II: Reaction mixture was cooled to 60 °C. Uninhibited butyl acrylate (36 mL) was purged

with nitrogen for 30 min in a slow addition funnel and slow added over 2 hours at 60 °C.

Reaction mixture was stirred for 2 hours at 60 °C and then was cooled to room temperature.

20   **Example XII**

Stage I: Water (200 mL), surfactant (Igepal CA-897 Octylphenol ethoxylate, Rhodia) (4.2 g.),

and initiator (0.1 g.) (2,2"-Azobis (N,N'-amidinopropane) dihydrochloride or V-50, Wako

chemicals) in a 4 necked round bottom flask were purged with nitrogen for 45 min. Uninhibited

styrene (21 mL) in a slow addition funnel was purged with subsurface nitrogen for 30 min. Reaction mixture was heated to 80 °C while stirring over 20 min. At room temperature styrene monomer slow addition was started and 5 mL styrene was slow added over 10 min before reaction temperature reached 80 °C and remaining monomer was slow added over 1.5 hours. At

5 the end of styrene slow addition, reaction mixture was stirred at 80 °C for 30 min.

Stage II: Reaction mixture was cooled to 60 °C. Uninhibited butyl acrylate (36 mL) was purged with nitrogen for 30 min in a slow addition funnel and slow added over 2 hours at 60 °C. Reaction mixture was stirred for 2 hours at 60 °C and then was cooled to room temperature.

10 For all given examples, samples were taken periodically to determine conversion, particle size, and molecular weight. Conversion was determined gravimetrically and molecular weight was determined using size exclusion chromatography on a Waters Associates system using Waters styragel columns and polystyrene standards. Particle size was determined for these examples using a Brookhaven Instruments BI90 or BI90plus particle size analyzer. The conversion,

15 molecular weight, and particle size data is given in Table I.

To extract homopolymer and polymer which is rich in one monomer, Soxhlet extraction was conducted on dried polymer using two different solvents based on the solubility of each polymeric component. Glass transition temperature of all residues was measured using a

20 Thermal Instruments Differential Scanning Calorimeter. Proton NMR was spectroscopy was conducted on all extracted and residue phases to determine composition using a Bruker NMR spectrometer. Soxhlet extraction results for example III are shown in Table II. The evolution of

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particle size with time for example 1 is shown in Figure I. GPC chromatograms of examples II, I, VII, and VIII are in Figures II, III, IV, and V respectively.

Table I. Conversion and molecular weight data for examples

Example	Overall Conversion		%Solids[1]	Particle Size (nm)		Molecular weight (Mn)[2]	
	Stage I	Final		Stage I	Final	Stage I	Final
I	83.21	95.93	36	36	45	28,000	1,136,000
II	73.56	66	25	127	61	25,000	120,000
III	75.7	64.38	23	-	84	18,000	2,476,000
IV	80.47	96.99	34	153	144	135,000	138,000
V	80.14	69.12	16	78	149.5	58,000	116,000
VI	82.54	86.36	20	63.7	553.8	1,539,000	1,580,000
VII	70.57	66.93	22	273	127	9,000	40,000
VIII	83.2	96	21	59	105	41,000	135,000
IX	76.4	81.5	23	53	88	11,000	1,458,000
X	94.2	81.9	30	21	67	15000	25,000
XI	89.75	36.66	9	57.7	91	77,000	52,000
XII	85.96	68.03	16	58.4	141.2	103,000	NA

Table II. **Soxhlet Extraction Results**

	Weight %	T_g °C				NMR mol% composition		
						BA	MMA	Styrene
Example III (Dried Polymer)	-	-55.98	-25.07	104		48.05	51.95	
Example III (Soxhlet Extraction in Acetone):								
flask	53	-54.7	-	103		54.8	45.2	-
thimble	-	-52.89	-	101		51.04	48.96	-
Example III (Soxhlet Extraction in ethyl acetate):								
flask	38.8	-54.09	-	117		48.33	51.67	-
thimble	8.2	-51.7	-	110		51.81	48.19	-

[1] Rounded to the nearest %
[2] Rounded to the nearest 1000 Daltons